

## Improved Synthesis of 1,3,5-Triarylbenzenes from $\alpha,\beta$ -Unsaturated Nitro Compounds

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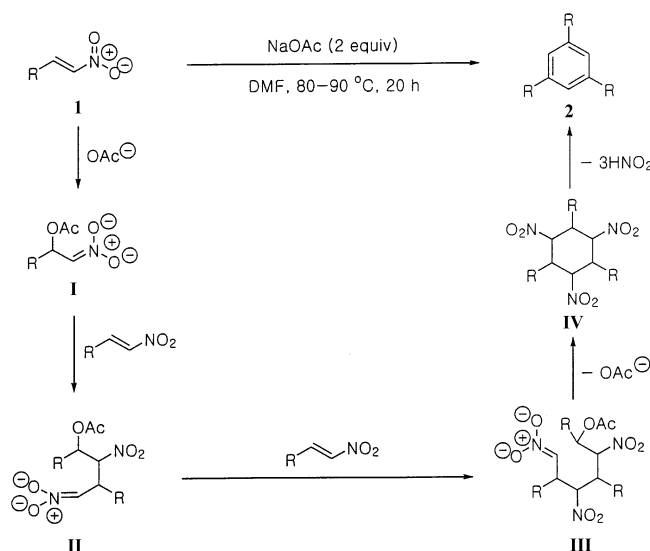
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Recently we have reported that *N,N*-dimethylformamide dimethylacetal (DMF-DMA) could be used as a useful initiator for the cyclic trimerization of  $\alpha,\beta$ -unsaturated nitro compounds to form 1,3,5-trisubstituted benzene derivatives.<sup>1</sup> In the reaction, trace amounts of methoxide ion in DMF-DMA might trigger the whole reaction.<sup>1,2</sup> However, the yields were not high enough to be practical in the synthetic point of view.<sup>3</sup>

Development of a new method for the preparation of 1,3,5-trisubstituted benzenes is important in view of their utility in the fields of electrode and electroluminescent devices<sup>4</sup> or in the chemistry of conducting polymers.<sup>5</sup> Most frequently used methods involve transition metal catalyzed cyclic trimerization of acetylene derivatives<sup>6</sup> and acid catalyzed trimerization of acetophenones.<sup>7</sup> In these contexts, we thought that the synthesis of 1,3,5-triarylbenzenes from  $\alpha,\beta$ -unsaturated nitro compounds is a new entity for the preparation of these valuable compounds.

Thus, in order to find more efficient catalyst for the cyclic trimerization of  $\alpha,\beta$ -unsaturated nitro compounds, we examined various candidates as a catalyst. These include sodium hydroxide, sodium methoxide, sodium acetate, potassium



Scheme 1

thioacetate, potassium cyanide, potassium iodide, potassium fluoride, and cesium fluoride *etc.* (see Table 1). We tried the reaction in DMF, DMSO, 1-methyl-2-pyrrolidinone (NMP), HMPA, methanol, and acetonitrile at rt -90 °C. Some representative trials were summarized in Table 1 by using  $\beta$ -nitrostyrene (**1a**) as a model substrate in various reaction conditions.

As shown in Table 1, we could obtain 1,3,5-triphenylbenzene (**2a**) in increased yield when we use sodium acetate as a catalyst in polar, aprotic solvent such as DMF, DMSO, NMP, and HMPA (entries 6, 14-16). Some variations of the reaction conditions such as reaction temperature, amounts of NaOAc, or reaction time did not improve the yield of **2a** significantly. Thus considering yields, amounts of side products, and ease of separation, we decide to use NaOAc in DMF as the best conditions in our trials (entry 6 in Table 1, Scheme 1).

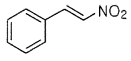
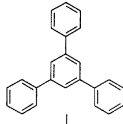
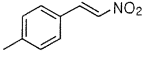
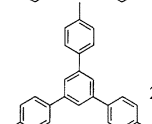
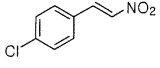
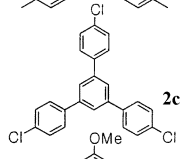
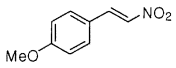
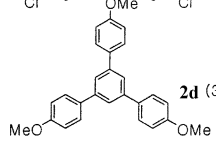
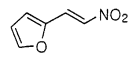
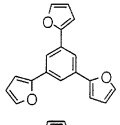
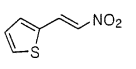
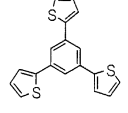
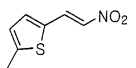
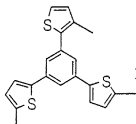
$\beta$ -Nitrostyrene derivatives **1a-d** or heterocyclic analogues **1e-g** afforded the corresponding trimerized compounds **2a-g** in 34-66% isolated yields. The results were summarized in Table 2. However, alkyl derivatives (eg, 1-nitro-3-methyl-1-butene or 1-nitro-1-cyclohexene) or  $\beta$ -substituted nitro olefins (eg, 1-nitro-1-methyl-2-phenylethene) did not give the desired products. The failure might be due to the steric hindrance of the intermediates, **II** or **III**, generated by the consecutive Michael addition reaction (*vide infra*).

The mechanism for the formation of **2** can be proposed as shown in Scheme 1. Addition of acetate ion to  $\beta$ -nitrostyrene

Table 1. Cyclic trimerization of **1a** in various reaction conditions

entry	solvent	initiator	reaction conditions	yield (%)
1	DMF	DMF-DMA (2 equiv)	80-90 °C, 20 h	34 (ref. 1)
2	DMF	NaOH (1 equiv)	80-90 °C, 20 h	low yield
3	DMF	MeONa (2 equiv)	80-90 °C, 20 h	low yield
4	MeOH	MeONa (2 equiv)	reflux, 40 h	no reaction
5	DMF	Me <sub>2</sub> NCH(OEt) <sub>2</sub> (2 equiv)	80-90 °C, 20 h	10
6	DMF	NaOAc (2 equiv)	80-90 °C, 20 h	40
7	DMF	KSAc (2 equiv)	80-90 °C, 20 h	low yield
8	DMF	KCN (2 equiv)	80-90 °C, 20 h	25
9	DMF	DABCO (2 equiv)	80-90 °C, 20 h	low yield
10	DMF	KI (4 equiv)	80-90 °C, 40 h	no reaction
11	DMF	Ph <sub>3</sub> P (1 equiv)	80-90 °C, 20 h	low yield
12	DMF	KF (2 equiv)	80-90 °C, 20 h	low yield
13	DMF	CsF (2 equiv)	80-90 °C, 20 h	36
14	DMSO	NaOAc (2 equiv)	80-90 °C, 24 h	41
15	NMP	NaOAc (2 equiv)	80-90 °C, 20 h	40
16	HMPA	NaOAc (2 equiv)	80-90 °C, 20 h	39
17	CH <sub>3</sub> CN	NaOAc (2 equiv)	reflux, 20 h	low yield
18	DMSO	KSAc (2 equiv)	80-90 °C, 20 h	low yield
19	DMF	NaOAc (2 equiv)	sonication, 60 °C, 20 h	29

**Table 2.** Synthesis of 1,3,5-triarylbenzene derivatives

entry <sup>a</sup>	$\beta$ -nitro styrene (1)	products (2, % yield) <sup>ef</sup>
1	 <b>1a</b>	 <b>2a</b> (40%) <sup>1,7a</sup>
2	 <b>1b</b>	 <b>2b</b> (37%) <sup>1,7a</sup>
3	 <b>1c</b>	 <b>2c</b> (34%) <sup>1,7a</sup>
4	 <b>1d</b>	 <b>2d</b> (35%) <sup>7b</sup>
5	 <b>1e</b>	 <b>2e</b> (40%) <sup>1</sup>
6	 <b>1f</b>	 <b>2f</b> (66%) <sup>1,7c</sup>
7	 <b>1g</b>	 <b>2g</b> (60%) <sup>7c</sup>

<sup>a</sup>All reactions were run on a 2 mmol scale.

gave a new nucleophilic intermediate **I**, which adds to  $\beta$ -nitrostyrene to give **II**. Subsequent addition, same reaction once again, cyclization, and the final elimination of nitrous acid afford the desired product.<sup>1,7f</sup> Lewis basic nature of DMF must facilitate the elimination of nitrous acid in the last step.

In this report we developed an improved practical preparation method of 1,3,5-triarylbenzenes from the easily available  $\alpha,\beta$ -unsaturated nitro compounds with the aid of sodium acetate in DMF.

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